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Published in:
Applied Physics Letters

DOI:
[10.1063/1.118542](https://doi.org/10.1063/1.118542)

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Document Version
Publisher's PDF, also known as Version of record

Publication date:
1997

[Link to publication in University of Groningen/UMCG research database](#)

Citation for published version (APA):

Inia, D. K., Propper, M. H., Arnoldbik, W. M., Vredenberg, A. M., & Boerma, D. O. (1997). Low-temperature nitriding of iron through a thin nickel layer. *Applied Physics Letters*, 70(10), 1245-1247.
<https://doi.org/10.1063/1.118542>

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Citation: *Appl. Phys. Lett.* **70**, 1245 (1997); doi: 10.1063/1.118542

View online: <https://doi.org/10.1063/1.118542>

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Low-temperature nitriding of iron through a thin nickel layer

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(Received 16 October 1996; accepted for publication 6 January 1997)

We present a new method for nitriding iron at low temperatures. First, iron is coated with a thin layer of nickel (~ 36 nm), after which it is exposed to an NH_3 atmosphere at temperatures below 300°C . Underneath the nickel layer $\epsilon\text{-Fe}_{3-x}\text{N}$ is formed at temperatures as low as 225°C , while uncovered iron samples show a large uptake of oxygen after the same treatment. The nickel layer prevents the oxidation of iron by impurities in the NH_3 gas, and acts as a catalyst for the decomposition of NH_3 . After decomposition the atomic nitrogen diffuses through the nickel layer towards the iron. With the process described, pore-free iron nitrides can be formed at low temperatures. © 1997 American Institute of Physics. [S0003-6951(97)04410-0]

The formation of a nitride layer in or on a ferritic surface layer leads to improvement of material properties like wear, fatigue and corrosion resistance. Besides these tribological and corrosion properties, the magnetic properties of iron nitrides have received a lot of attention recently. Nitride layers can consist of various nitrides among which $\epsilon\text{-Fe}_{3-x}\text{N}$ and $\gamma'\text{-Fe}_4\text{N}$ are the most important ones. The nitrogen chemical potentials of the various iron nitrides are higher than the chemical potential of nitrogen in N_2 gas at normal pressures. This means that iron nitrides are metastable in air at 1 atm. They decompose into Fe and N_2 at temperatures above 400°C . Surface nitride layers can be formed in an ambient with a very high nitrogen chemical potential, which can be provided by, for instance, a mixture of NH_3 and H_2 . Which nitride is formed depends on the temperature and on the nitriding potential of the gas mixture defined by $p_{\text{NH}_3}/p_{\text{H}_2}^{3/2}$, where p_{NH_3} and p_{H_2} denote the partial pressures of NH_3 and H_2 , respectively. Temperatures used in this process are usually between 500 and 650°C . Due to the thermodynamic instability of the formed nitride phases, the nitride layers usually exhibit a high degree of porosity. Already during formation of the layer, the nitride partially decomposes and pores develop, due to the formation of high pressure N_2 bubbles.¹ The degree to which the formed nitride layers decompose at larger depth in the layer depends on the kinetics of the reactions. By increasing the rate of formation relatively to that of decomposition, it should be possible to diminish or even prevent the formation of N_2 bubbles. Just applying a lower nitriding temperature does not work, however. Although at temperatures lower than 400°C the decomposition of the nitrides is kinetically hindered, the growth of nitrides is also extremely slow, or nitrides do not form at all at these temperatures under nitriding conditions used in practice. In this letter we will show that the kinetic barriers for iron nitride formation can be lowered by applying a thin Ni layer on top of iron, so that the temperature range for nitriding of Fe can be extended to temperatures below 300°C . Dissociation of NH_3 at the Ni surface, fol-

lowed by diffusion of N through the Ni layer leads to the formation of a nitride layer behind the interface which, due to the fact that the decomposition rate of nitrides is practically zero at these temperatures, is pore-free.

In a previous study of N implantation in Ni/Fe bilayers we showed that it is possible to introduce nitrogen in iron by implanting the nitrogen in a 100 nm top layer of nickel.² After implantation in Ni, the N atom diffuses from Ni into the Fe layer, where a nitride is formed. This was explained using an enthalpy diagram for N in Ni/Fe bilayers, in which the formation enthalpies of the nitrides and the heats of solution of nitrogen in both metals were taken into account. Both values are slightly lower for Fe than for Ni, so that there is a chemical driving force for the nitrogen to diffuse towards the Fe layer.

In the present work, Ni and Fe layers were subsequently deposited on Si in a vacuum of 10^{-6} Pa by means of e-beam evaporation. Thicknesses of the layers were 36 nm for the Ni layer and 240 nm for the Fe layer as measured by means of Rutherford backscattering spectrometry (RBS). Also samples consisting of thick Fe (1 mm) covered with 40 nm Ni were used. After transport through air, nitriding was done in an ammonia atmosphere (99.9995% pure). Nitriding temperatures were below 300°C . At these temperatures, interdiffusion of Ni and Fe does not occur, as revealed by RBS.

Depth profiles of nitrogen and oxygen in nitrided samples were measured with elastic recoil detection (ERD), using an incoming beam of Ag ions with an energy of 72 MeV, at an incident angle of 25° with the surface plane. Outcoming particles were detected in a dE-E telescope at a recoil angle of 37° , corresponding to an angle of 12° with the surface plane. Details of this technique, which yields energy spectra from which depth profiles can be deduced for light elements such as H, C, N and O separately, are given elsewhere.³ Structural analysis was performed by x-ray diffraction (XRD) using Cu K_α radiation in a θ - 2θ geometry and also by Mössbauer spectroscopy.

A Ni/Fe bilayer on Si was heated to 275°C in pure NH_3 at 1 atm for 30 min. In Fig. 1(a) the depth profiles up to 200 nm (the ERD probing depth) of nitrogen and oxygen are shown. The Ni/Fe interface is indicated by a bar. In the iron layer, the nitrogen has reached a maximum concentration of ~ 33 at. % at the interface, which slowly decreases with depth. These high N concentrations indicate the forma-

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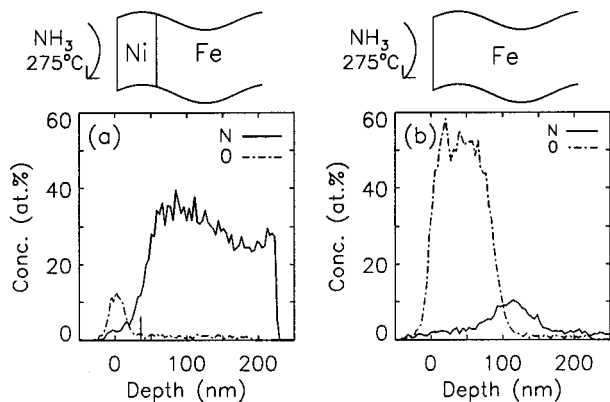


FIG. 1. N and O depth profiles after treatment at 275 °C in NH_3 : (a) Ni/Fe bilayer and (b) Fe layer.

tion of ϵ -nitride, which has a composition range of 25–33 at. % N. Only a few at. % N is present in the Ni layer. A small oxygen peak is seen at the surface of the sample. ERD measurements on the as deposited sample revealed that this peak was also present before nitriding. The presence of the ϵ phase was confirmed by XRD. The diffractogram [Fig. 2(c)] shows peaks which can all be ascribed to $\epsilon\text{-Fe}_{3-x}\text{N}$, apart from a peak due to Ni with a possible contribution from $\alpha\text{-Fe}$. In Fig. 1(b) nitrogen and oxygen depth profiles of an uncovered layer of iron treated under the same conditions are shown. Here only a small amount of N is present underneath a layer with an oxygen concentration of ~ 50 at. % indicating the formation of an iron oxide layer.

It is obvious from these figures that Fe samples with a Ni top layer show a completely different behavior in a NH_3 atmosphere at 275 °C as compared to samples without a Ni layer. Samples with a Ni layer form nitrides, while samples without a Ni layer predominantly oxidize.

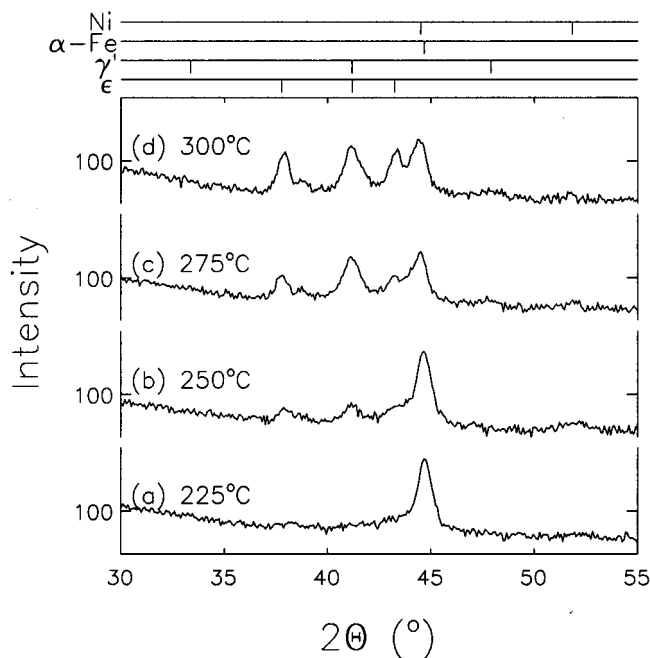


FIG. 2. XRD spectra of Ni/Fe bilayers nitrided in NH_3 at: (a) 225 °C, (b) 250 °C, (c) 275 °C and (d) 300 °C.

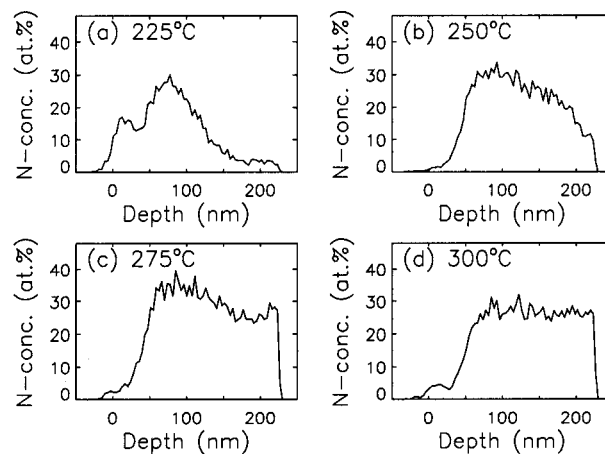


FIG. 3. N concentration depth profiles of Ni/Fe bilayers nitrided in NH_3 at: (a) 225 °C, (b) 250 °C, (c) 275 °C and (d) 300 °C.

In Fig. 3, the N profiles obtained after nitriding at 225, 250, 275, and 300 °C during 30 minutes are shown. In all cases, a concentration of ~ 30 at. % is measured at the interface and a more or less decreasing concentration towards deeper regions can be seen. At 225 °C, a ~ 3 at. % level is seen beyond ~ 150 nm, probably due to an $\alpha'\text{-Fe(N)}$ phase or N adsorbed at grain boundaries, which was also seen in the implantation experiments.² XRD measurements at the samples treated at 250–300 °C [Figs. 2(b)–2(d)] show that, apart from a peak from Ni and/or $\alpha\text{-Fe}$ at 44.51° , all peaks are consistent with formation of ϵ , although from the peak at 41.19° and the lump at $\sim 48^\circ$, the presence of a small amount of $\gamma'\text{-Fe}_4\text{N}$ cannot be excluded. The diffraction peaks due to the ϵ phase are not clearly observed for the sample prepared at 225 °C [Fig. 2(a)]. However, from Mössbauer spectroscopy it was found that at this temperature ϵ -nitride is also present.

These observations may be explained as follows. For the case of Ni-covered Fe, the NH_3 will dissociate at the Ni surface. A major fraction of the N atoms thus created is taken up in the Ni layer. Another fraction will recombine to N_2 . From our present data it is clear that no nickel nitrides are formed, at least not at temperatures above 250 °C. The atomic N diffuses towards the underlying Fe layer and forms a nitride. It is clear from the peaks in the N concentration below the Ni/Fe interface that at least a part of the nucleation of nitrides takes place preferentially near the interface. A decreasing nitrogen profile might occur due to different growth rates in different grains or to additional nucleation of nitrides in deeper parts of the Fe layer. From experiments not presented here, we have indications that in other cases nitride particles do not nucleate preferentially at the interface but are present throughout the Fe layer. These differences in nucleation behavior possibly arise from differences in impurities and structure at the interface.

The question arises why the nitriding reaction with Fe is so much slower in the absence of a Ni layer. From literature we did not find a large difference between the dissociation rates of NH_3 at clean Fe and Ni surfaces.^{4,5} Most likely therefore, the difference in nitriding rates arises from a difference in the oxidation behavior of Ni and Fe. It is clear

from our data that the formation of an oxide layer on iron cannot be prevented, even when ultra-pure NH_3 gas is used. The contaminant level of O_2 or H_2O in the gas was estimated to be 5–10 ppm, which is apparently enough for the oxidation of Fe, while it is insufficient for the formation of a nickel oxide layer. Moreover, it is known that the reduction rate of Ni is two to three orders of magnitude larger than that of Fe in hydrogen at pressures of 10^{-4} – 10^{-2} Pa,^{6,7} and that thick iron oxide layers cannot be reduced by H_2 at low pressures.⁸ Below the iron oxide layer in the uncovered sample a small amount of nitrogen is found. Presumably, in the initial stage some N uptake occurs after which the surface continues oxidizing and the N accumulates at the oxide-iron interface. Such an effect has also been observed in the oxidation of iron nitrides.⁹ The iron oxide layer may prevent or diminish the dissociation of NH_3 at the surface.

We showed that it is possible to form nitride layers in iron at temperatures below 300 °C by applying a thin Ni layer on top of the iron. At these temperatures the decomposition of the nitrides into Fe and N_2 is very slow, which means that pores in the nitride layer do not form in contrast with nitriding processes at higher temperatures. This leads to better material properties.¹⁰ The Ni layer acts as a catalytic surface for the decomposition of ammonia and at the same time it prevents the iron from oxidation. After transport through the Ni layer, nitrogen enters the Fe layer and nitrides are formed. In this work, we formed nitride layers of approximately 250 nm on Si. In other experiments on bulk Fe samples with a Ni layer, it was shown that it was also possible to form nitride layers. Obviously, the nitriding conditions were such that nucleation of iron nitrides prevails over long-range diffusion of N in Fe.

Besides the possible industrial application of this method for low temperature nitriding of iron (a patent application has been submitted), it also provides us with an opportunity to study the Fe–N phase diagram at temperatures below

350 °C, where only little is known about this phase diagram. For instance, the existence of the triple point at ~ 315 °C between α -Fe, γ' - Fe_4N and ϵ - Fe_{3-x}N can be studied under equilibrium conditions. For the existence of this triple point some evidence has been given in experimental work and thermodynamical calculations.^{11–13}

The authors would like to thank Ing. F. van der Horst and Professor Dr. L. Niesen from Groningen University for performing the XRD and Mössbauer spectroscopy experiments, respectively, and the FOM Institute for Atomic and Molecular Physics (AMOLF) for providing the evaporation facilities. This work was performed with financial support from the Stichting voor Fundamenteel Onderzoek der Materie (FOM) and the Stichting Technische Wetenschappen (STW).

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